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On the Location of Cobalt Ions in Co-Y Zeolites

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The location of cobalt ions in Co-Y zeolites has been discussed. Electronic spectra of Co-Y have a weak maximum at 530 nm at a hydrated state and three maxima at 530, 590, and 650 nm at dehydrated states. Magnetic measurements have revealed that effective magnetic moments of a cobalt ion are 5.2 and 4.4–4.7 BM in a hydrated and dehydrated Co-Y, respectively. From these results, it is concluded that Co ions are located in an octahedral field at a hydrated state. At dehydrated states, Co ions should be located in a tetrahedral field and hence not in S_1 site which are the most favorable site for alkaline and alkaline earth ions. Infrared spectra of Co-Y adsorbing pyridine have allowed to discuss the location of Co ions in more detail.

1. INTRODUCTION

The catalysts developed from synthetic zeolites have been found to be effective for a variety of reactions.¹⁾ Original zeolite contains Na ions as cations to neutralize the negative charge produced by AlO_4 tetrahedra and the Na ions can be exchanged with other various kinds of cations. In the last decade, the zeolites exchanged with alkaline earth and rare earth ions have been found to act as solid acid catalysts. Recent topics of zeolite catalysts seem to be the catalysis by zeolites exchanged with transition metal ions. Physico-chemical properties of the zeolites are investigated in detail in the case of the zeolites exchanged with alkaline or alkaline earth ions, but for the transition metal ion-exchanged forms, the systematic investigations are not carried out in so many cases.

It is very important to clarify the location of cations in the zeolites for elucidation of the catalytic action of the zeolites. The investigations on this line are few. Barry and Lay²⁾ reported on the basis of ESR measurements that Mn ions are distributed in zeolites in a different manner from Ca ions. The location of Cu ions in Cu-Y zeolite is also reported.³⁾ Olson⁴⁾ carried out the X-ray diffraction analysis of nickel faujasite, but there is no report on X-ray analysis of Co-Y zeolite.

Recently, we found that Co-Y reveals solid acidity and is an effective catalyst for isomerization of 1-butene.⁵⁾ To clarify the catalytic action of the zeolite, we started the investigation on the location of Co ions in Co-Y. In the course of the investigation, Stone *et al.*⁶⁾ reported on the location of Co ions by means of magnetic susceptibility measurements. Their argument was based on magnetic measurements only. It seems that their conclusion should be examined by another methods. We have measured reflectance electronic spectra, infrared spectra, solid acidity as well as magnetic susceptibility of various kinds of Co-Y and discussed the location of Co ion in Co-Y.

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zeolites in the present work.

2. EXPERIMENTAL

1. Samples

Linde Y zeolite (SK-40, Na-Y) was impregnated with a cobalt nitrate solution of a given concentration. The solution was refluxed at the boiling point for 8–10 hr and filtered. X-ray diffraction patterns of the samples revealed no change in the crystal structure of the zeolite frameworks by the procedure. After water content of the dried zeolite was determined by a Shimadzu micro electric thermanobalance MTB-50, an aliquot was dissolved in a nitric acid solution and the content of cobalt ions was analyzed by EDTA titration.

2. Apparatus and Procedure

Electronic spectra. — About 1 g of sample was put into a quartz cell of 1 mm thickness and evacuated at a given temperature for 3 hr. Diffuse reflectance spectra of the sample of different evacuated states were taken on a Shimadzu MPS-50L spectrometer.

Magnetic measurements. — Magnetic susceptibilities of powdered samples were determined over the temperature range 77–273°K on a Shimadzu M2B variable temperature Faraday balance system calibrated with Mohr salt. About 50 mg sample

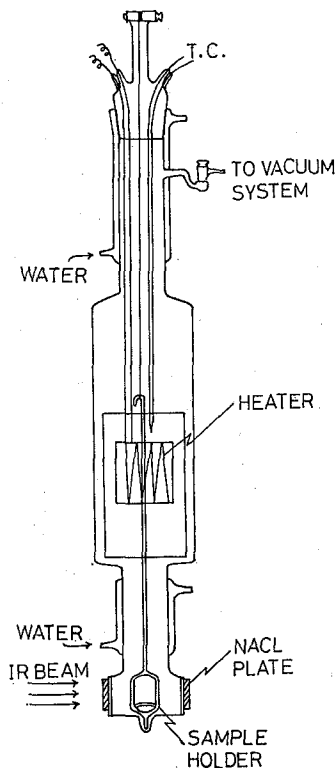


Fig. 1. IR cell for adsorption measurement.

was evacuated and loaded into a small pyrex glass ampoule in vacuo, and then sealed. Corrections for Na-Y zeolite and the glass ampoule were made by the data which were obtained in blank tests.

Infrared spectra. — A 10–20 mg sample was pressed to a disk of 20 mm diameter and put into a cell as shown in Fig. 1. Infrared spectra of the sample evacuated at a given temperature or adsorbing pyridine were recorded in situ by a JASCO IRA-2 grating spectrometer.

Acidity measurements. — Solid acidity of a Co-Y was determined by the titration method after Tamele⁷⁾ using butter yellow ($pK_a = +3.3$) as an indicator.

Isomerization of 1-butene. — A 130 mg of Co-Y was put into a 24.5 ml glass reactor and evacuated at 400°C for 3 hr. 1-butene of 1×10^{-4} mol was introduced to the reactor at 100°C. After 10 seconds, the butene was recovered into a nitrogen trap and analyzed by gaschromatography.

3. RESULTS

1. Electronic Spectra

At a hydrated state, Co-Y was pink and became blue by evacuation at temperatures higher than 200°C. When the evacuated Co-Y was allowed to stand in contact with the atmosphere, the color reverted to pink. In general, the color change was very similar to each other for the Co-Y over wide range of degree of exchange. The behavior shows the change of a crystal field acting on Co ions and was investigated by electronic spectroscopy in detail.

Figure 2 shows electronic spectra of 68% exchanged Co-Y. At completely hydrated state, a weak absorption maximum at 525 nm was observed (Curve A). When the sample was evacuated at 400°C for 3 hr, there were clear three absorption maxima with large absorbance in the spectrum (D). The sample evacuated at 250°C gave

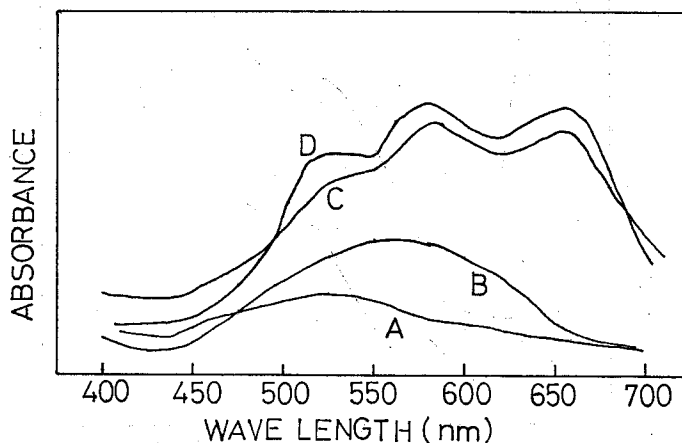


Fig. 2. Electronic spectra of 68% exchanged Co-Y zeolite.

- A; The Co-Y completely hydrated.
- B; D after contact with the atmosphere for a short time.
- C; The Co-Y evacuated at 250°C.
- D; The Co-Y evacuated at 400°C.

a similar spectra but in this case the three maxima became a little obscure as shown in the figure (C). Curve B in the figure was obtained for the sample D which was contacted with the atmosphere for a short time. The spectrum resembles curve A as a whole, though a weak broad absorption overlapped on curve A. The spectrum identical to Curve A was obtained for the sample after a long time contact with the atmosphere. Hence, the change of spectra by dehydration is reversible.

In Table I, observed values of absorption maxima (λ_{\max}) are shown for 4 kinds of Co-Y. It is evident from the Table that λ_{\max} s were not affected by the degree of exchange of Na ions by Co ions.

As Co-Y zeolite is an effective catalyst for isomerization of 1-butene as described later, electronic spectra of the Co-Y adsorbing 1-butene were recorded. Figure 3 shows the change of the spectrum of 50% exchanged Co-Y (Co content, 1.07 mmol/g)

Table I. Absorption Band Maxima (λ_{\max}) in Electronic Spectra of Co-Y Zeolites

degree of exchange	operation	λ_{\max}		
9%	in the atmosphere	530		
	evacuation at 250°C	535	590	655
	evacuation at 400°C	540	595	660
32%	in the atmosphere	530		
	evacuation at 200°C	540	580	635
	evacuation at 400°C	540	580	635
68%	in the atmosphere	525		
	evacuation at 250°C	530	580	660
	evacuation at 400°C	530	580	660
80%	in the atmosphere	520		
	evacuation at 200°C	535	585	655
	evacuation at 400°C	535	585	660

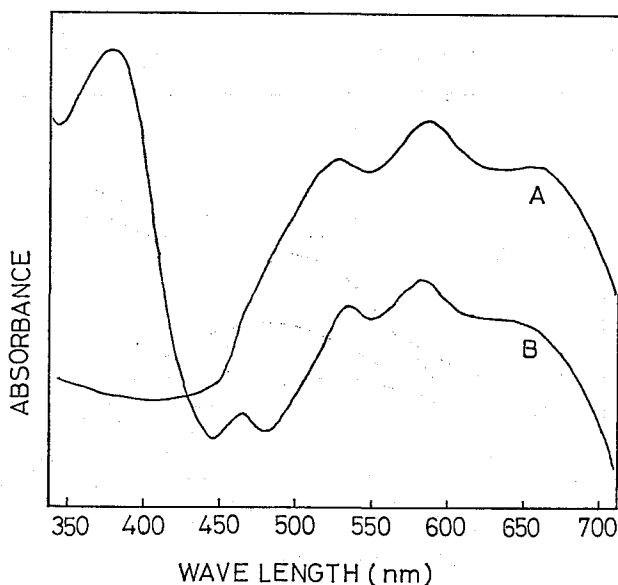


Fig. 3. Electronic spectra of Co-Y adsorbing 1-butene.

A; 50% exchanged Co-Y evacuated at 400°C.

B; A adsorbing 1-butene at 70°C followed by evacuation at 150°C for 1hr.

by adsorbing 1-butene. Curve B in the figure was obtained for the sample which adsorbed 3 mmol/g of 1-butene at 70°C followed by evacuation at 150°C for 1 hr. A strong absorption band at 380 nm and a weak one at 465 nm appeared by the operation. On the other hand, no change was observed in the wave length region of 530–650 nm.

2. Infrared Spectra of Adsorbed Pyridine

It has been established by Parry⁸⁾ and Ward⁹⁾ that infrared spectra of pyridine adsorbed on solid acids offer the reliable information about the surface properties of the solids. Characteristic absorption bands appear upon the adsorption of pyridine on Broensted acid sites, Lewis sites (trigonally coordinated aluminum ions) and cations. It can be distinguished by inspection of the spectra whether Co ions can adsorb pyridine or not.

The infrared spectra adsorbed on evacuated Na-Y and Co-Y are shown in Figs. 4 and 5. Ward⁹⁾ reported 1625 (w), 1610 (w), 1588 (s), 1570 (w), 1492 (m), and 1438 (m) cm^{-1} bands for pyridine adsorbed on Na-Y and attributed them to coordinately

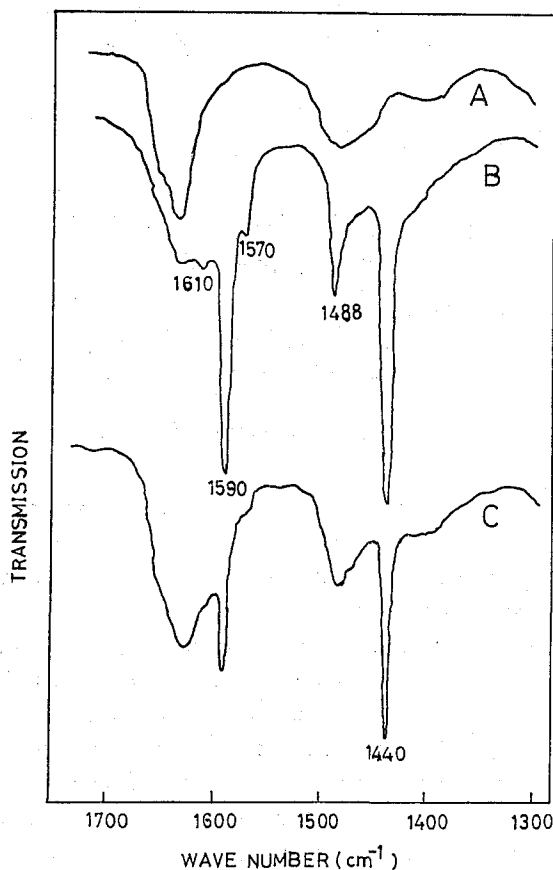


Fig. 4. IR spectra of Na-Y adsorbing pyridine.

A; The Na-Y evacuated at 300°C for 3 hr.

B; A adsorbing pyridine at room temperature at 3 Torr.

C; B evacuated at 200°C for 30 min after standing overnight.

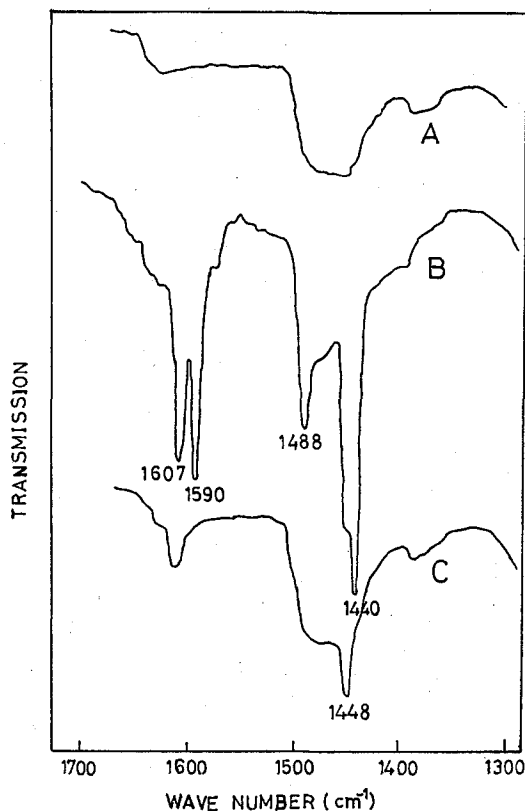


Fig. 5. IR spectra of Co-Y adsorbing pyridine.

- A; 48% exchanged Co-Y evacuated at 450°C for 4 hr.
- B; A adsorbing pyridine at 0.5 Torr followed by evacuation at room temperature for 15 min.
- C; B evacuated at 200°C for 30 min after standing overnight at room temperature.

bound pyridine. By inspecting the spectra for various alkaline metal exchanged zeolite, he showed the 1438 band is characteristic to pyridine interacting with Na ions. In Fig. 4 all bands reported by Ward except 1625 band are observed and these bands decreased in its intensity by 200°C evacuation.

When pyridine was adsorbed on Co-Y (48% exchanged), additional bands appeared at 1448 and 1607 cm^{-1} . The additional bands remained after 200°C evacuation, though other bands due to pyridine interacting with Na ions disappeared in this case. The fact shows that 1448 and 1607 bands can be assigned to pyridine interacting with Co ions and the interaction is stronger than that between pyridine and Na ions. Ward¹⁰⁾ already reported without original spectra the appearance of 1446 cm^{-1} band for a Co-Y zeolite of highly exchanged and assigned it to pyridine coordinated to Co ions. But in the paper, the very close band frequencies were reported for Mn, Ni, Zn, Cu, and Cd-Y zeolites, for example, 1446 for Co and 1447 for Cd-Y. Hence, 1446 band seems to be not definite evidence of interaction between pyridine and Co ions. A strong band of 1607 cm^{-1} should be considered as the evidence

rather than 1446 band.

3. Magnetic Susceptibility

Magnetic susceptibilities of 31.8% and 79.6% exchanged Co-Y were measured for hydrated and evacuated states. For each samples, a linear plot of $1/\chi$ versus T was obtained over the temperature range of 100°–270°K. From the gradient of the line, effective magneton numbers μ_{eff} were calculated using the following equation,

$$\mu_{\text{eff}} = 2.83\sqrt{58.9C}$$

where C is Curie constant. The results are shown in Table II. At a hydrated state, μ_{eff} was 5.2 for both samples and at evacuated states, μ_{eff} were in the range of 4.4–4.7.

Table II. Effective Magneton Numbers of Co-Y Zeolites

degree of exchange	operation	μ_{eff}
31.8%	in the atmosphere	5.2 ₃
	evacuation at 200°C	4.7 ₅
	evacuation at 400°C	4.4 ₄
79.6%	in the atmosphere	5.1 ₈
	evacuation at 200°C	4.6 ₇
	evacuation at 400°C	4.6 ₅

Stone *et al.*⁶⁾ reported μ_{eff} of 80% exchanged Co-Y. In the paper, the value of 3.94 is cited for the sample dehydrated at 475°K, but for other samples dehydrated over the temperature range of 295–655°K, μ_{eff} are reported to be in the range of 4.65–5.06 which are in good agreement with the present results.

4. Acidity

Na-Y showed no acidity but when Na ions are exchanged with Co ions, solid acidity appeared. Figure 6 shows the change of acidity with the degree of exchange. All samples were evacuated at 400°C for 3 hr and put into a 0.1 N butylamine in cyclohexane solution. For the transfer of the samples from a vacuum system to the solution, the samples were contacted with the atmosphere for a very short time (about several seconds) and hence a little amount of water might be adsorbed.

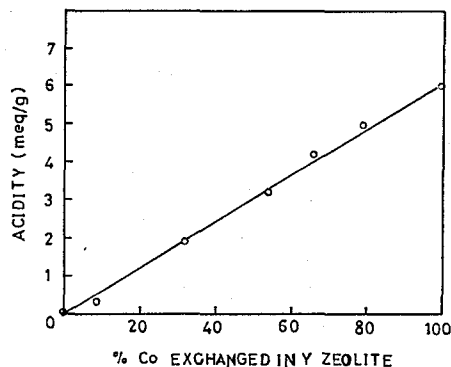


Fig. 6. Acidity of Co-Y zeolites measured by a titration method using butter yellow as an indicator.

As shown in the figure, the acidity increase linearly with the degree of exchange. This trend is different from that in the case of Cu-Y zeolite. A concave curve was obtained for acidity change in Cu-Y zeolites.¹¹⁾

5. Isomerization of 1-butene

The conversion of 1-butene at 100°C was measured for Co-Y of various degree of exchange. The catalysts were pre-evacuated at 400°C for 3 hr. As shown in Fig. 7, the activity varied almost linearly with Co content in contrast with the isomerization by Cu-X. Dimitrov and Leach¹²⁾ reported the remarkable increase in activity by exchange of Na ions with Cu ions more than 40%. When the catalysts were pre-evacuated at 250°C, the higher activities by 6~7 times were observed showing incomplete dehydration to be favorable for the isomerization.

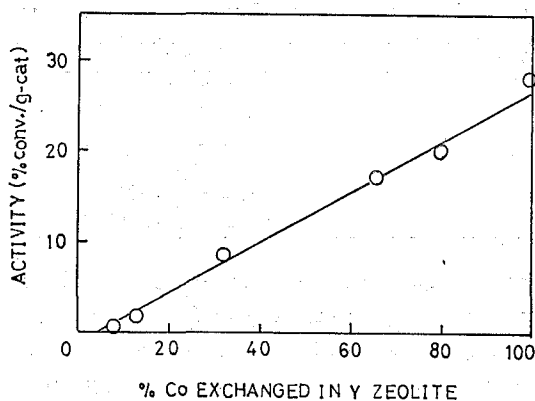


Fig. 7. Catalytic activity of Co-Y zeolites in isomerization of 1-butene at 100°C.

4. DISCUSSION

1. Coordination State of Co Ions

Stone *et al.*⁶⁾ concluded that Co ions are in an octahedral field at a hydrated state and a tetrahedral field at dehydrated states. The present work confirmed their conclusion by further evidences, especially by electronic spectra. Many works have been carried out on the electronic spectra of Co (II) compounds of octahedral and tetrahedral coordination. In solutions, for example, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ shows a weak absorption band at 530 nm with a molar extinction coefficient (ϵ) of about 10 and $[\text{CoCl}_4]^{2-}$ shows three strong bands at 600–700 nm with the strongest band of 680 nm, the ϵ of which is about 600.¹³⁾ For Co ions in solids, Poppalardo and others¹⁴⁾ investigated the spectra of Co ions doped in MgO. The spectrum which has an absorption maximum at 510 nm is very similar to Fig. 2-A in the present work and they assigned it to Co ions in an octahedral field. On the other hand, Weakliem and McClure¹⁵⁾ reported that Co ions doped in ZnO give a spectrum having maxima at 660, 620, and 570 nm. The bands are assigned to Co ions in a tetrahedral field.

By comparison of Fig. 2 and Table I with the investigations mentioned above, it is evident that Co ions in hydrated Co-Y are in an octahedral field and the circumstance of a Co ion should be like that of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. By dehydration, coordina-

tion state of Co ions change from the octahedral to a tetrahedral coordination. The coordination states are independent of Co content in the zeolites. Furthermore, no significant difference was observed for the samples evacuated at different temperatures above 200°C, as shown in Table I. As molar extinction coefficient of 530 nm band is very small, for the dehydrated Co-Y, there is a possibility of existence of the 530 nm band which is hidden by overwhelming absorption bands with large ϵ due to tetrahedrally coordinated Co ions.

In order to have an information about degree of dehydration, the weight loss of Na-Y by heating was measured by a micro thermanobalance. The result is shown in Fig. 8. The weight loss measured in the atmosphere and the temperature was raised with a rate of 7°/min. In the measurement of electronic spectra of Co-Y, the sample was evacuated at a given temperature for 3 hr. Therefore, the degree of dehydration of the evacuated sample should be much larger than that in the figure at the same temperature. Thus, the sample evacuated at 400°C for 3 hr can be safely said to be in the completely dehydrated state, while by evacuation at 200° or 250°C, some residual water might remain in the zeolite and the 530 nm band due to octahedrally coordinated Co ions might superpose in the absorption bands by tetrahedral Co ions. The slight difference between Figs. 2-C and D can be understood as the effect resulted from the residual water.

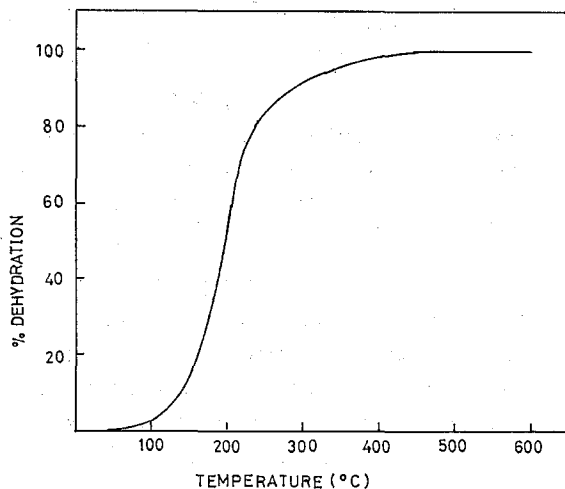


Fig. 8. Dehydration of Na-Y as a function of temperature. The temperature was raised at a rate of 7°C/min.

The above discussion is supported by the magnetic susceptibility measurements. For octahedrally coordinated Co ions of high spin type, μ_{eff} are reported to be 4.7–5.7 and for tetrahedral one to be 4.2–4.7.¹⁶⁾ The obtained values cited in Table II correspond well to the conclusion deduced from electronic spectra. The value 4.75 for 31.8% exchanged sample evacuated at 200°C would reflect the incomplete dehydration.

In general, the result obtained here confirms the observation by Stone *et al.*

2. Location of Co Ions in Co-Y Zeolite

Several sites are proposed for location of cation in Y zeolites. Figure 9 shows a schematic view of a part of the zeolite. S_I site is in a hexagonal prism connecting two sodalite units and is surrounded by six oxygen octahedrally. There are 16 S_I sites in a unit cell while 32 S_{II} and 48 S_{III} sites which are in a supercage and surrounded by 3 and 2 oxygen, respectively. Another sites S_I' , S_{II}' , and S_{III}' are proposed which are in a sodalite unit and just opposite to S_I , S_{II} , and S_{III} . A S_I site can accommodate all divalent cation, if the degree of exchange is less than 58%. Other sites mentioned above can accommodate all divalent cation without limit of degree of exchange. By X-ray analysis, the S_I site is proved to be the most favorable site for Ca ion.¹⁷⁾ Acidity and activity pattern of Cu-Y zeolite¹²⁾ suggest that exchange of ions by Cu ions begin at the S_I site.

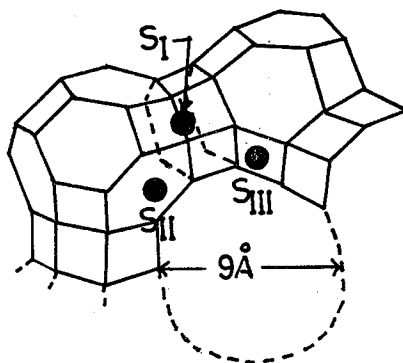


Fig. 9. A schematic view of Y zeolite. A dotted circle line shows a supercage. Polyhedra show sodalite units and hexagonal prism connecting two adjacent sodalite units. A S_I site exists in a hexagonal prism. S_{II} and S_{III} sites exist in the supercage.

In the case of Co-Y zeolite, in contrary, the present work shows the S_I site is not the most favorable one for the location of Co ions, as Co ions exist in a tetrahedrally coordinated state in the dehydrated Co-Y with very small Co content. Acidity and activity change with Co content support the above discussion. If S_I site is a favorable position of Co ions, the acidity, which is clearly associated with Co ions, should not change linearly with Co content as in the case of Cu-Y. Thus Co ions should be located on the other sites.

In hydrated Co-Y, Co ions are octahedrally coordinated. As S_I are not considered to be the accommodation sites of Co ions, the plausible species are those of $\text{Co}(\text{H}_2\text{O})_6$, $\text{Co}(\text{H}_2\text{O})_4(\text{Ox})_2$, and $\text{Co}(\text{H}_2\text{O})_3(\text{Ox})_3$ where (Ox) stands for an oxygen of aluminosilicate frameworks. First two species are allowed to exist only in a supercage, while the latter is allowed in both sodalite unit and supercage. Distinction of these can not be made from the results obtained here. It is conceivable that all of these coexist in the hydrated Co-Y.

In dehydrated Co-Y, Co ions are tetrahedrally coordinated. Aluminosilicate frameworks can not afford themselves tetrahedral coordination sites. Coordination of S_I' , S_{II} , and S_{III}' sites are normally trigonal but cobalt ions in S_I' and S_{III}' can adopt

a tetrahedral coordination if there is a fourth oxygen near the center of the sodalite unit which is a part of a residual water molecule of a hydroxyl group derived from such a molecule, as already pointed out by Stone *et al.*⁶⁾ Ward¹⁸⁾ reported that hydroxyl groups are persistent to dehydration in zeolites, hence a hydroxyl group as a fourth ligand is plausible in Co-Y evacuated at 400°C.

Spectroscopic study of adsorbed molecules afford a more detailed information about the location of Co ions. The electronic spectrum of adsorbed 1-butene (Fig. 3) shows no change in the coordination state of Co ions. New bands at 380 and 465 nm are very similar to that reported by Webb¹⁹⁾ for adsorbed 1-butene on silica-alumina. He assigned the bands to a π or charge transfer complex formed by the olefine double bond acting as an electron donor and the acid proton as an acceptor. Thus 1-butene is considered not to be adsorbed on Co ions directly.

On the other hand, infrared spectra of adsorbed pyridine revealed the interaction between Co ions and pyridine molecules. These phenomena can be explained if the location of Co ion is assumed to be a $S_{II'}$ site. The $S_{II'}$ site is just inside of a sodalite window open to a supercage. Water molecule can pass through the window but not 1-butene, hence 1-butene can not coordinate to Co ions. Pyridine molecule can also not pass the window but pyridine is much stronger base than 1-butene, Co ions may move to S_{II} sites from $S_{II'}$ sites and direct interaction with pyridine will occur. A S_I' site is far inside of a sodalite unit and there will be a considerably high potential barrier between the site and other sites in a supercage.

In conclusion, most of Co ions in the dehydrated Co-Y zeolite will be located in $S_{II'}$ sites. The conclusion is consistent with that given by Stone *et al.*⁶⁾

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S. YOSHIDA, M. NAKAJIMA, K. NAITO, Y. KOSHIMIDZU, and K. TARAMA

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